

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 1 – Notes: Enthalpy and Bond Energies

**Objectives:** Explain the relationship between energy and heat.  
Identify, define, and explain: thermochemistry, energy, heat, endothermic, exothermic, chemical potential energy.  
Determine the approximate enthalpy of a formation reaction with bond energies.

**Text Reference:** Section 11.1 – pages 293-299 & part of Section 11.2 – pages 300-306

**Energy:**

**Work ( $W$ ):**

**Heat ( $q$ ):**

**Temperature ( $T$ ):**

Every sample of matter has energy stored in it. From where does this stored energy in matter come?

The total of all these forms of energy is called **heat content**, or the **ENTHALPY**, of the substance. The symbol for enthalpy is  **$H$** .

**Enthalpy ( $H$ ):**

In all chemical reactions, there is a **change in enthalpy** ( $\Delta H$ ). The total enthalpy of the products is different from the total enthalpy of the reactants. *Remember, change in enthalpy is the enthalpy of the final products minus the enthalpy of the reactants.*

**Endothermic:**

In order for a process to absorb heat, what must be true of the initial reactant versus the final products?

What is true of the change in enthalpy of an endothermic process?

**Exothermic:**

In order for a process to release heat, what must be true of the initial reactant versus the final products?

What is true of the change in enthalpy of an exothermic process?

**Heat of reaction ( $\Delta H$ ):**

**Molar heat of formation ( $\Delta H_f$ ):**

Compounds with **positive** or **low negative values** of heats of formation are generally . . .

Example:  $\Delta H_f$  of  $\text{H}_2\text{S} = -4.82$  kcal/mol;  $\Delta H_f$  of  $\text{HI} = +6.33$  kcal/mol

Compounds with **high negative values** of heats of formations are very . . .

Example:  $\Delta H_f$  of  $\text{CO}_2 = -95.05 \text{ kcal/mol}$

Compounds with **high positive values** of heats of formation are very . . .

Example:  $\Delta H_f$  of  $\text{HgC}_2\text{N}_2\text{O}_2$  (mercury fulminate) = 64 kcal/mol

The standard enthalpy of formation ( $\Delta H_f^\circ$ ) of any element in its standard state is **ZERO**.

**Standard conditions** for thermodynamic processes are generally 1 atm of pressure and 25°C.

Standard conditions are indicated by placing a  $^\circ$  next to the quantity.

$\Delta H_f$  = heat of formation but  $\Delta H_f^\circ$  = standard heat of formation

**Heat of combustion ( $\Delta H_c$ ):**

*Enthalpy changes for reactions can be obtained by simply subtracting the heats of formation of the reactants from the heats of formation of the products. Be sure to multiply the heats of formation by the coefficient of the compound involved.*

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}}$$

**Example 1:** Find the enthalpy ( $\Delta H_r^\circ$ ) for the reaction:  $\text{CuO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Cu}_{(s)} + \text{H}_2\text{O}_{(g)}$

It is important to remember to specify the state of a substance when its  $\Delta H_f$  is listed since different states of the same substance have different heat contents. Remember, heat is absorbed or released when a substance changes state:  $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$   $\Delta H = 6.01 \text{ kJ}$

How do compounds have energy of formation? If elements have no energy of formation, how does a compound have an energy?

**Bond dissociation energy:**

In order to break bond . . .

When bonds are formed . . .

Let's look at some bond dissociation energies:

|       |          |       |          |       |         |
|-------|----------|-------|----------|-------|---------|
| H - H | 436.4 kJ | O = O | 498.7 kJ | H - C | 414 kJ  |
| H - O | 460. kJ  | C - C | 347 kJ   | C = C | 620. kJ |

**Example 2: Ethene Hydrogenation:** What is the approximate  $\Delta H_r^\circ$  for the following reaction:  $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$ ?  
From where does the  $\Delta H_r^\circ$  for this reaction come? Most of the energy of the reaction comes from its bond energies.

**Example 3:** Calculate the approximate  $\Delta H_f^\circ$  for the formation of water:  $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$

**Question:** How do you designate *standard* conditions?

**Question:** What are standard conditions?

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 1 – Assignment: Enthalpy and Bond Energies

Answer the following questions.

1. When chemical bonds are broken, energy is \_\_\_\_\_ but when they are formed energy is \_\_\_\_\_.
2. For exothermic reactions,  $\Delta H$  values are (+) / (-). For endothermic reactions,  $\Delta H$  values are (+) / (-).
3. Distinguish between these various forms of energy: chemical potential energy, work, and heat.
4. A system is a person and the system is next to a campfire. Is this system endothermic or exothermic? Explain.
5. A system is a person who is perspiring. Is this system endothermic or exothermic? Explain.
6. Circle the letter(s) of the true statements below.
  - a. Energy is detected only because of its effects.
  - b. Heat is energy that transfers from one object to another because they are at the same temperature.
  - c. Heat flows from a cooler object to a warmer object.
  - d. If two objects remain in contact, heat will flow from the warmer to the cooler until their temperatures are the same.
  - e. When a substance dissolves in water, heat is always released.
  - f. The sign of  $\Delta H$  is negative for an exothermic reaction.
  - g. If 129 kJ of heat is required to decompose 2 mol  $\text{NaHCO}_3$ , then 258 kJ is required to decompose 1 mole.
  - h. In endothermic reactions, the energy of the product(s) is higher than the energy of the reactants.
7. The value for  $\Delta H_f^\circ$  for magnesium nitride is listed as  $-461$  kJ/mol. This means that the enthalpy of 1 mole of the  $\text{Mg}_3\text{N}_2$  is 461 kJ **GREATER** / **LESS** than the sum of the enthalpies of Mg and  $\text{N}_2$
8. The value of  $\Delta H_f^\circ$  for ethane is listed as 52.3 kJ/mol. This means that the enthalpy of 1 mole of  $\text{C}_2\text{H}_6$  is 52.3 kJ **GREATER** / **LESS** than the sum of the enthalpies of C and  $\text{H}_2$ .
9. For the reaction:  $2 \text{HgO}_{(s)} \rightarrow 2 \text{Hg}_{(s)} + \text{O}_{2(g)}$  the  $\Delta H_r$  is +43.4 kcal. What is the  $\Delta H_f$  for  $\text{HgO}$ ?
10. The  $\Delta H_c$  for one mole of ethyl alcohol is -227 kcal. How much heat is evolved when 11.5 g of ethyl alcohol is combusted? First you need to write a reaction...
11. The following are some  $\Delta H_f$  values:  $\text{CH}_{4(g)} = -17.9$  kcal/mol;  $\text{CHCl}_{3(l)} = -31.5$  kcal/mol;  $\text{HCl}_{(g)} = -22.1$  kcal/mol  
What is the heat of reaction for the equation:  $\text{CH}_{4(g)} + 3 \text{Cl}_{2(g)} \rightarrow \text{CHCl}_{3(l)} + 3 \text{HCl}_{(g)}$
12. Calculate the heat of reaction for the decomposition of sodium chlorate:  $\text{NaClO}_{3(s)} \rightarrow \text{NaCl}_{(s)} + 3/2 \text{O}_{2(g)}$   
 $\Delta H_f$  for  $\text{NaClO}_3 = -85.7$  kcal/mol;  $\Delta H_f$  for  $\text{NaCl} = -98.2$  kcal/mol

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 2 – Notes: Thermochemistry and Hess' Law (and a Little Entropy)

**Objectives:** Identify, define, and explain: thermochemistry, system, surroundings, universe, endothermic, exothermic, Hess' Law, isobaric, isothermal, and Hess' Law.  
Use Hess' Law to calculate/determine the enthalpy changes in chemical and physical processes.  
Calculate enthalpy changes using standard heats of formation.  
Explain the relationship between the system and the surroundings and the flow of heat between the two.

**Text Reference:** Section 11.1 – pages 292-299 & Section 11.4 – pages 314-318

**Introductory Question:** Natural systems tend to go from a state of higher energy to a state of lower energy. What does this mean with respect to endothermic and exothermic reactions? Then, why do endothermic reactions take place at all?

#### Thermodynamics:

Recall, change in enthalpy is the change in the heat content of a system at a constant pressure.

##### Isobaric:

##### Isothermal:

If you keep the temperature constant, then the change in energy of the system is in the form of work on or by the system.

##### System:

##### Surroundings:

##### *System + Surroundings = Universe*

Heat flowing from the system to the surroundings is . . .

Heat flowing from the surroundings to the system is . . .

What happens when two objects come in contact?

Is there another way to determine the energy of a reaction without knowing the heats of formation for the components? Yes!!!

**Hess' Law:** the enthalpy change for a reaction is the sum of the enthalpy changes for a series of reactions that add up to the overall reaction.

In other words: *When a reaction can be expressed as the algebraic sum of two or more other reactions, then the enthalpy is the algebraic sum of the heats of formation of these other reactions.*

**Example 1:** Find the enthalpy ( $\Delta H_r$ ) for the reaction:  $\text{CuO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Cu}_{(s)} + \text{H}_2\text{O}_{(g)}$

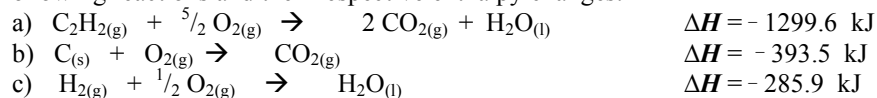
We can find:

|  |                                   |
|--|-----------------------------------|
| $\text{Cu}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{CuO}_{(s)}$         | $\Delta H_f = -37 \text{ kcal}$   |
| $\text{H}_{2(g)} + 1/2 \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}$ | $\Delta H_f = -57.8 \text{ kcal}$ |

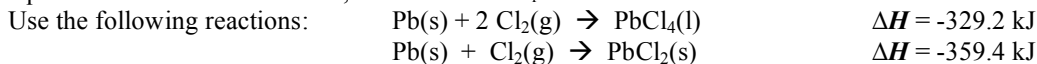
**Example 2:**

Calculate the  $\Delta H$  for the reaction:  $2 \text{C}_{(s)} + \text{H}_{2(g)} \rightarrow \text{C}_2\text{H}_{2(g)}$

Use the following reactions and their respective enthalpy changes:

**Example 3:**

Liquid lead (IV) chloride is formed by the reaction of solid lead (II) chloride with gaseous chlorine. Write an equation for this reaction. Then, calculate the  $\Delta H_r$ .



Just as a short introduction to the next topic, let's have a quick overview of a property called **ENTROPY**.

**Entropy (S):**

Something with perfect order would have no disorder and would have  $S = 0$ .

What would have ZERO ENTROPY?

Is there anything at these conditions?

What does this mean with regard to entropy values of substance?

Think about the entropy of solids, liquids, and gases.

|                    |          |                  |                 |
|--------------------|----------|------------------|-----------------|
| Crystalline solids | pattern: | degree of order: | entropy values: |
| Liquids            | pattern: | degree of order: | entropy values: |
| Gases              | pattern: | degree of order: | entropy values: |

Is the entropy of a substance very significant and useful to us?

What is significant to us with regard to entropy?

How do you find the change in entropy?

$$\Delta S = \sum \Delta S_{(final\ state)} - \sum \Delta S_{(initial\ state)}$$

What if a reaction has a positive value for  $\Delta S$ ? What is an example of such a process?

What is a reaction has a negative value for  $\Delta S$ ? What is an example of such a process?

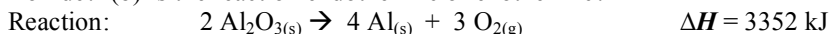
What do you think is the most likely thing to happen: increase in entropy or decrease in entropy?

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 2 – Assignment: Thermochemistry and Hess' Law

1. What can be considered the “system” and what are considered the “surroundings” when studying a mixture of chemicals undergoing a reaction? How is the flow of heat described?

2. A considerable amount of heat is required to is required for the decomposition of aluminum oxide. (a) What is the  $\Delta H_f$  for aluminum oxide? (b) Is the reaction endothermic or exothermic?



3. Find the  $\Delta H_r$  for the reaction  
Use the following information:

$$\begin{array}{l} \text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \\ \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) \\ \frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \end{array} \quad \begin{array}{l} \Delta H_f = 90.4 \text{ kJ/mol} \\ \Delta H_f = 33.6 \text{ kJ/mol} \end{array}$$

4. Find the  $\Delta H_r$  for the reaction  
Use the following information:

$$\begin{array}{l} 2 \text{P}(\text{s}) + 5 \text{Cl}_2(\text{g}) \rightarrow 2 \text{PCl}_5(\text{s}) \\ \text{PCl}_5(\text{s}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \\ 2 \text{P}(\text{s}) + 3 \text{Cl}_2(\text{g}) \rightarrow 2 \text{PCl}_3(\text{g}) \end{array} \quad \begin{array}{l} \Delta H = 87.9 \text{ kJ} \\ \Delta H = -574 \text{ kJ} \end{array}$$

5. What is the  $\Delta H_f$  for  $\text{PCl}_5(\text{s})$  from the above problem?

6. The combustion for ethene is as follows:  $\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$   $\Delta H = -1390 \text{ kJ}$   
Calculate the amount of heat liberated when 4.79 g ethane reacts with excess oxygen.

7. Find the  $\Delta H_r$  for the reaction  
Use the following information:

$$\begin{array}{l} \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) \\ 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \\ \text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + 2 \text{CO}_2(\text{g}) \\ 2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 6 \text{H}_2\text{O}(\text{l}) + 4 \text{CO}_2(\text{g}) \end{array} \quad \begin{array}{l} \Delta H = -572 \text{ kJ} \\ \Delta H = -1401 \text{ kJ} \\ \Delta H = -3100 \text{ kJ} \end{array}$$

8. Diborane, ( $\text{B}_2\text{H}_6$ ) is a highly reactive boron hydride, which was once considered as a rocket fuel in the U.S. space program. Calculate  $\Delta H$  for the synthesis of diborane from its elements, according to the equation:  $2 \text{B}(\text{s}) + 3 \text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g})$

Use the following data:

$$\begin{array}{l} \text{(a)} \quad 2 \text{B}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ} \\ \text{(b)} \quad \text{B}_2\text{H}_6(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 3 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -2035 \text{ kJ} \\ \text{(c)} \quad \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -286 \text{ kJ} \\ \text{(d)} \quad \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = 44 \text{ kJ} \end{array}$$

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 3 – Notes: Entropy, Free Energy, & Spontaneity

**Objectives:** Identify, define, and explain: free energy, spontaneity, entropy, nonspontaneous reaction, spontaneous reaction, law of disorder, and Second Law of Thermodynamics.  
Calculate the change in entropy of a reaction or process and explain its significance with regard to spontaneity.  
Calculate the free energy for a reaction or process and explain its significance to spontaneity.  
Identify and define conditions where a reaction will be spontaneous, nonspontaneous, or in equilibrium.  
Describe how enthalpy change and entropy change may work together or against one another in conjunction with temperature to determine the spontaneity or nonspontaneity of a reaction.

**Text Reference:** Section 19.3 – pages 549-556

#### Introductory Questions:

What is entropy?

What does a positive value of  $\Delta S$  indicate?

What does a negative value of  $\Delta S$  indicate?

What is the more likely situation: an increase in entropy or a decrease in entropy?

**Second Law of Thermodynamics:** There are many versions of the second law, but all describe the directionality of the universe

Version 1: *It is impossible to completely convert heat into work without some other changes in the universe.*

Version 2: *Heat will not of itself flow from a colder to a hotter body.*

Version 3: The most general statement of the second law of thermodynamics: *The entropy of the universe is increasing.*

#### Sock Drawer Example:

Sock drawers do get organized and water can be decomposed into hydrogen and oxygen and refrigerators transfer heat from a colder to a hotter body. All of these are “unnatural” events – **nonspontaneous** in the vocabulary of thermodynamics. *They will not occur by themselves; they require that work be done by someone or something.* An input of energy is necessary to reduce the entropy and increase the order. And in every case, the work that is done generates more entropy somewhere in the universe than it reduces in one small part of the universe. Even when entropy appears to decrease in a **spontaneous** change that occurs “by itself,” for example, the freezing of water at temperature below 0°C, there are balancing increases in entropy. In this particular case, the heat given off by the freezing water adds to the disorder of its surroundings. In short, when the entire universe is considered, entropy always increases.

#### Spontaneous reaction:

#### Nonspontaneous reaction:

In terms of ENTHALPY:

spontaneous/favorable:

nonspontaneous/unfavorable:

In terms of ENTROPY:

spontaneous/favorable:

nonspontaneous/unfavorable:

Do endothermic reactions occur? YES. Do reactions happen where there is a decrease in entropy? YES!  
So how do these two properties come together to determine if a reaction will be spontaneous or not?

**Free Energy or Gibbs Free Energy:** the energy of a system that is available to do work

This relationship between enthalpy and entropy was discovered by American scientist William Gibbs, and he showed the effect of entropy depends upon the temperature. The **Gibbs Equation** is:

$$\Delta G = \Delta H - T \Delta S$$

$\Delta H$  = change in enthalpy;  $T$  = temperature in kelvin;  $\Delta S$  = change in entropy

The Gibbs Free Energy Equation shows that the  $T\Delta S$  of a system is equivalent to the amount of heat that must be transferred to produce a given change of entropy,  $\Delta S$ , at the temperature  $T$ .

Gibbs showed that a change is spontaneous **ONLY** if the change in free energy,  $\Delta G$ , is **NEGATIVE**. It is not enough for  $\Delta H$  to be **NEGATIVE** for a change to be spontaneous. It is not enough for the  $\Delta S$  to be **POSITIVE** for a change to be spontaneous.

For a reaction to be spontaneous, the combination of  $\Delta H$  and  $-T \Delta S$  must be **NEGATIVE**, indicating a release of total free energy.

For a reaction to be spontaneous, the change in the free energy must be . . .

For a reaction that is nonspontaneous, the change in free energy is . . .

If the change in free energy is ZERO, . . .

**Example 1:** For a given reaction,  $\Delta H = -37$  kcal,  $\Delta S = -0.060$  kcal/K, and  $T = 300^\circ\text{C}$ . Calculate the  $\Delta G$  at  $300^\circ\text{C}$ .

Since  $\Delta G$  is \_\_\_\_\_, the change \_\_\_\_\_ take place spontaneously at  $300^\circ\text{C}$ .

**Example 2:** Use the above values for the reaction occurring at a temperature of  $400^\circ\text{C}$ . Calculate  $\Delta G$ .

Since  $\Delta G$  is \_\_\_\_\_, the change \_\_\_\_\_ take place spontaneously at  $400^\circ\text{C}$ .

**KEY NOTE:** The whole notion of free energy tells us that there are two factors that favor a reaction: a decrease in energy in the form of enthalpy and an increase in disorder. If these two factors are working against each other, then temperature will determine which is the more dominant factor – the higher the temperature, the more entropic considerations override enthalpic ones. Note: Also, the implication that a reaction that is favorable at one temperature may not be favorable at another.

Because the temperature is always positive, i.e., in Kelvin, the effects of the signs of  $\Delta H$  and  $\Delta S$  and the effect of spontaneity can be summarized in the following table.

Let's examine four different situations.

| <i>Situation</i> | <i>Signs of <math>\Delta H</math> and <math>\Delta S</math></i> | <i>Comment</i> |
|------------------|---|----------------|
| 1                | $\Delta H = -$ (favorable)<br>$\Delta S = +$ (favorable)        |                |
| 2                | $\Delta H = +$ (unfavorable)<br>$\Delta S = -$ (unfavorable)    |                |
| 3                | $\Delta H = -$ (favorable)<br>$\Delta S = -$ (unfavorable)      |                |
| 4                | $\Delta H = +$ (unfavorable)<br>$\Delta S = +$ (favorable)      |                |

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 3 – Assignment: Entropy, Free Energy, & Spontaneity

Complete the assignment on a separate sheet of paper. You do not have enough room to squeeze your work into the space here.

- For a certain reaction,  $\Delta H = -22$  kcal and  $\Delta G = -12$  kcal at  $25^\circ\text{C}$ . (a) Calculate the  $\Delta S$ . (b) For the same reaction, calculate  $\Delta G$  when the temperature is  $227^\circ\text{C}$ .
- The  $\Delta H$  for a certain reaction is  $-30.0$  kcal and the  $\Delta S$  is  $0.080$  kcal/K. (a) Calculate the  $\Delta G$  at  $25^\circ\text{C}$ . (b) Will this reaction occur spontaneously at  $500$ . K? Explain how you know. (c) Is this an endothermic or exothermic reaction? Explain how you know.
- Explain, by calculating  $\Delta G$ , why KCl crystals will dissolve in water at  $25^\circ\text{C}$ , although the  $\Delta H$  is positive. (You need to use some words in your explanation to indicate why the  $\Delta G$  is significant.) NOTE:  $\Delta H = +2.0$  kcal;  $\Delta S = +0.023$  kcal/K
- For the phase change,  $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$ , the value of  $\Delta H$  is  $1440$  cal/mole. The  $\Delta S$  value is  $5.26$  cal/mol K. Calculate  $\Delta G$  and state whether the change is spontaneous at (a)  $+10.0^\circ\text{C}$  and (b)  $-10.0^\circ\text{C}$ . (c) Is the reaction endothermic or exothermic? Explain how you know.
- Determine whether the following reaction is spontaneous:  $\text{C}_{(s)}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$   
 $\Delta H = -393.5$  kJ/mol       $\Delta S = +0.0030$  kJ/K mol       $T = 298.15$  K
- Predict the sign of  $\Delta S^\circ$  for each of the following reactions:  
 a. The thermal decomposition of solid calcium carbonate:  $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$   
 b. The oxidation of  $\text{SO}_2$  in air:  $2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g)$
- Calculate the  $\Delta S^\circ$  at  $25^\circ\text{C}$  for the reaction:  $2 \text{NiS}(s) + 3 \text{O}_2(g) \rightarrow 2 \text{SO}_2(g) + 2 \text{NiO}(s)$   
 Use the following standard entropy values:  
 $\text{SO}_2(g)$      $S^\circ = 248$  J/mol K       $\text{NiO}(s)$      $S^\circ = 38$  J/mol K  
 $\text{NiS}(s)$      $S^\circ = 53$  J/mol K       $\text{O}_2(g)$      $S^\circ = 205$  J/mol K
- Calculate  $\Delta S^\circ$  for the reduction of aluminum oxide by hydrogen gas:  $\text{Al}_2\text{O}_3(s) + 3\text{H}_2(g) \rightarrow 2 \text{Al}(s) + 3 \text{H}_2\text{O}(g)$   
 Use the following standard entropy values:  
 $\text{Al}_2\text{O}_3(s)$      $S^\circ = 51$  J/mol K       $\text{H}_2(g)$      $S^\circ = 131$  J/mol K  
 $\text{Al}(s)$      $S^\circ = 28$  J/mol K       $\text{H}_2\text{O}(g)$      $S^\circ = 189$  J/mol K
- Consider the reaction:  $2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g)$  carried out at  $25^\circ\text{C}$  and  $1$  atm. Use the following data:  
 $\text{SO}_2(g)$      $\Delta H^\circ = -297$  kJ/mol       $\Delta S^\circ = 248$  J/mol K  
 $\text{SO}_3(g)$      $\Delta H^\circ = -396$  kJ/mol       $\Delta S^\circ = 257$  J/mol K  
 $\text{O}_2(g)$      $\Delta H^\circ = 0$  kJ/mol       $\Delta S^\circ = 205$  J/mol K  
 (a) Calculate  $\Delta H^\circ$ .  
 (b) Calculate  $\Delta S^\circ$ .  
 (c) Calculate  $\Delta G^\circ$ .  
 (d) Is the reaction endothermic or exothermic? How do you know?  
 (e) Is the reaction spontaneous at  $25^\circ\text{C}$ ? How do you know?
- Given:  
 a.  $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{NaCl}(s)$        $\Delta H^\circ = -93.23$  kcal  
 b.  $\text{H}_2(g) + \text{S}(s) + 2 \text{O}_2(g) \rightarrow \text{H}_2\text{SO}_4(l)$        $\Delta H^\circ = -193.91$  kcal  
 c.  $2 \text{Na}(s) + \text{S}(s) + 2 \text{O}_2(g) \rightarrow \text{Na}_2\text{SO}_4(s)$        $\Delta H^\circ = -330.50$  kcal  
 d.  $\frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{HCl}(g)$        $\Delta H^\circ = -22.06$  kcal  
 (a) Find the  $\Delta H_r$  for the following chemical change:  $2 \text{NaCl}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{Na}_2\text{SO}_4(s) + 2 \text{HCl}$   
 (b) Is the reaction endothermic or exothermic? How do you know?
- Calculate the enthalpy of combustion ( $\Delta H_c$ ) for the reaction in which ethane combines with oxygen to form carbon dioxide and water. Use the following information:  
 $2 \text{C}(s) + 3 \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$        $\Delta H = -20.2$  kcal  
 $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$        $\Delta H = -94.0$  kcal  
 $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$        $\Delta H = -57.8$  kcal

## Chapter 11: Thermochemistry – Heat and Chemical Changes

### Part 4 – Notes: Calorimetry and Calculations

**Objectives:** Identify, define, and explain: calorimetry, calorimeter, enthalpy, thermochemical equation, heat of reaction, heat of combustion, adiabatic, and isothermal.  
Construct equations that show heat changes for chemical and physical processes.  
Calculate heat changes and/or temperatures or temperature changes for chemical or physical changes.

**Text Reference:** Section 11.2 – pages 300-306

A calorimeter is a piece of equipment in which a reaction is performed *adiabatically* (or *isothermally*) meaning no heat flow is able to occur. The energy of the reaction is kept inside the calorimeter and not allowed to escape into the environment. Using the calorimeter, the heat involved in a reaction may be determined. This is how the calories (or Calories) of food is determined. Foods are combusted in calorimeters and their heat content is determined.

Often, a sample with a higher temperature is added to a material of lower temperature. After the system equilibrates, the temperature of the two substances is the same. Many calculations are done based on this premise. When a “colder” substance is added to a “warmer” substance, certain things are true. Let’s point out some things. (pardon me if these seem obvious.)

1. The “colder” substance will increase in temperature (heat energy “flows” into it). The “warmer” substance will decrease in temperature (heat energy “flows” out of it).
2. The whole mixture will wind up at the **SAME** temperature that is higher than the low temperature but lower than the high temperature.
3. The energy that was lost by the warmer substance (“flowed” out of the warmer temperature) is equal in energy but opposite in sign to the energy that was absorbed by the cooler substance (“flowed” in to the cooler substance).

Let’s look at a typical problem that would be done and how to take these things into account.

**Example 1:** A piece of iron with a mass of 21.5 g at a temperature of 100.°C is dropped into a calorimeter containing 132 g of water at an initial temperature of 20.0°C. The specific heat of iron is  $C_p = 0.448 \text{ J/g}^\circ\text{C}$ . The specific heat of water is 4.184 J/g°C. What is the final temperature of the system/mixture?

*Recall, the heat lost by the iron has the same absolute value as the heat gained by the water.*

**Example 2:** Determine the final temperature when 18.0 g of ice at  $-10.0^\circ\text{C}$  mixes with 275.0 g of water at  $60.0^\circ\text{C}$ . For water:  $C_{\text{fus}} = 334 \text{ J/g}$ ,  $C_{p \text{ liquid}} = 4.184 \text{ J/g}^\circ\text{C}$ , and  $C_{p \text{ ice}} = 2.060 \text{ J/g}^\circ\text{C}$ .

**Example 3:** 32.2 g of water at  $14.9^\circ\text{C}$  mixes with 32.2 g of water at  $46.8^\circ\text{C}$ . What is the final temperature of the mixture? The specific heat of water is 4.184 J/g°C.

